Reaction Sintered Zircon-Dolomite Compositions for Insulating Refractories

A thesis submitted in the partial fulfilment of the requirements

for the degree of Bachelor of Technology

By

Chirag Saigal

109CR0209

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CERTIFICATE

This is to certify that the thesis entitled, "**Reaction Sintered Zircon-Dolomite Compositions for Insulating Refractories**" submitted by **Mr. Chirag Saigal (109CR0209)** in partial fulfilments for the requirements for the award of Bachelor of Technology degree in Ceramic Engineering at National Institute of Technology, Rourkela is an authentic work carried out by him under my supervision and guidance.

To the best of my knowledge, the matter embodied in this thesis has not been submitted to any other University/Institute for the award of any Degree or Diploma.

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LIST OF ABBREVIATIONS

1. XRD – X-Ray Diffraction.

2. AP – Apparent Porosity.

3. BD – Bulk Density.

4. CCS – Cold Crushing Strength

5. SEM – Scanning Electron Microscope.

6. Z-2 – 20% Zircon + 80% Dolomite.

7. Z-4 – 40% Zircon + 60% Dolomite.

8. Z-6 – 60% Zircon + 40% Dolomite.

9. Z-8 – 80% Zircon + 20% Dolomite.

ABSTRACT

Insulating refractories are used to increase the thermal/fuel efficiency of high temperature processes. Higher degree of porosity and pores with uniform size and even distribution increases the insulating properties of a refractory material. Zircon and Dolomite are used as raw materials for preparing of insulating bricks because their mixture, when sintered results in making of a highly porous material with good strength. Also, since no combustible material (pore formers) is used, the process of manufacturing do not results in formation of any harmful gases and thus is environment friendly. Densification studies like Apparent Porosity and Bulk Density of the fired samples was done. Cold Crushing Strength was also determined. Phase analysis was done by X-Ray Diffraction method to get an idea about various phases of Ca-Si-Zr-Mg formed after sintering. Microstructural analysis on the fractured surfaces was done by Scanning Electron Microscope to observe the pore morphology and distribution.

CHAPTER 1

INTRODUCTION

1. INTRODUCTION

Insulating refractories, as the name suggests are mainly used for insulating purposes in industrial applications now a days. These are highly porous, have low thermal conductivity and heat capacity than any other refractories commercially available [1]. Insulating refractories increase the thermal / fuel efficiency of the overall production process by preventing loses due to conduction of heat and thus are widely used in crowns of glass furnaces, tunnel kilns or as back-up linings of furnaces. Porosity is usually created by burning out a combustible material that is either present or is added to the raw material mixture. As the combustible material burns out during firing, a large fraction of pores is created within the fired body. However, the insulating property or the thermal conductivity of the final product depends not only upon the total porosity, but also upon the pore morphology, i.e. size, shape and distribution of the pores [2,3].

Silica-bonded magnesia materials are known to have high thermal expansion coefficient along with poor thermal spalling resistance. When combined with X_2O_3 ($X = Cr^{+3}$, Al^{+3}), the thermal shock resistance of the material is improved [4, 5]. However, due to environmental protection regulations, which ban the use of chrome-based materials [6], we use zircon in order to form $CaZrO_3$ based materials. Zircon and Dolomite are very economical raw materials for the production of $CaZrO_3$-Ca_2SiO_4-MgO materials [7]. Dicalcium silicate (Ca_2SiO_4) have five polymorphs, amongst which the (β) orthorhombic to (γ) monoclinic transformation is very similar to that of the tetragonal to monoclinic transformation observed in ZrO_2, i.e. both

experience expansion on transformation during cooling. However, there exist differences between these two corresponding transformations. Firstly, in Ca_2SiO_4, the transformation occurs from a β microstructure (twinning) to a γ structure that is untwined, while in ZrO_2 the reverse phenomenon occurs. Secondly, unlike in ZrO_2, the transformation from β to γ is irreversible, as β is a metastable phase. Thirdly, the volume expansion associated with phase transformation is 12% for Ca_2SiO_4, while it is just 4.9% for ZrO_2 (at room temperature) [8]. Zircon (ZrO_2) and Dolomite ($MgCa(CO_3)_2$) were used to produce $CaZrO_3$-Ca_2SiO_4-MgO based materials according to the following reaction:

$ZrO_2 + 3\ MgCa(CO_3)_2 \rightarrow 3MgO + CaZrO_3 + \beta\text{-}Ca_2SiO_4 + 6CO_2(g)$.

In preparation of Zircon-Dolomite based insulating refractories, no pore formers like saw-dust were used; hence the process do not releases any combustible or harmful materials during the firing process and is environment friendly.

CHAPTER 2

LITERATURE REVIEW

2. LITERATURE REVIEW

2.1 Zircon [9]

Zircon ($ZrSiO_4$) is mined for use as special foundry sands, refractories, abrasives, etc. It is produced as a co-product of heavy mineral mining. It is considered as a good refractory material for the following reasons:-

- Low coefficient of thermal expansion.
- High Melting Point.
- Chemical Inertness.
- Compatibility with new chemical binders.

Generally Zircon consists of 67% Zirconia, 32% Silica, with about 1% Hafnium. Zircon is extremely resistant to both mechanical and chemical attacks and is non-magnetic as well as a non-conductor. Use of Zircon as a refractory requires low interstitial water content. Zircon does not contain volatile elements that produce gases on heating. Zircon sand is generally mixed with pre-fired zircon, zircon flour and bonding agents, to extend the life of ladle linings upto 5-10 times than that of alumina brick linings.

2.2 Dolomite

Dolomite or $(Ca,Mg)(CO_3)_2$ have trigonal rhombohedral crystal symmetry. It constitutes of about 30% $CaCO_3$ and about 20% $MgCO_3$ normally. Loss on ignition or LOI is very high (~50%). Density is about 2.8. On heating to 700-900^oC, it loses CO_2 and thus is converted to Calcium Oxide and Magnesium Oxide mixtures known as caustic dolomite.

2.3 Insulating Refractories

High-temperature processes require a considerably high amount of energy. Often, input energy in these high-temperature processes is only partially used for the actual technical process and more than 30 to 40% energy escapes through the walls and out of the system. To optimize the use of energy and to prevent its escape into the ambience, special materials called insulating refractories are necessary. The main function of insulating refractory is to reduce the rate of heat flow (heat loss) through the walls of furnaces. Insulation is improved by providing a layer of material having low heat conductivity so that heat does not readily pass through them [10]. The desirable feature of insulating refractories is high degree of porosity which results in low thermal conductivity. However, the thermal conductivity of the insulating refractories does not depend on the size of pores but on the uniformity of size and even distribution of these pores. Thus, small-sized uniformly distributed pores are preferred.

2.4 Zircon-Dolomite Compositions

Heat treatment of Zircon-Dolomite compositions results in [11-17]

- In between 1000-1200^{o}C, i.e. initial stages following reactions take place:

  $\{CaO + MgO\} + ZrSiO_4 \rightarrow Ca_3Mg(SiO_4)_2 + t\text{-}ZrO_2 + MgO + \text{Amorphous Phases}$.

  $t\text{-}ZrO_2 + \text{Amorphous Phases} \rightarrow CaZrO_3 + \text{Amorphous Phases}$.

  $Ca_3Mg(SiO_4)_2 + \text{Amorphous Phases} \rightarrow CaSiO_4 + \text{Amorphous Phases}$.

- Rearrangement and neck formation.
- Neck growth, grain growth, shrinkage, pore phase.
- Final Stage Sintering.

Porosity of 30% or above is observed after sintering [18-24].

CHAPTER 3

EXPERIMENTAL

3. EXPERIMENTAL

3.1 Sampling of Raw materials

Raw materials used in the preparation of test samples were:-

Batch compositions are as follows (Table-1):-

BATCH COMPOSITION		
Sample	Zircon (wt. %)	Dolomite (wt. %)
Z-2	20	80
Z-4	40	60
Z-6	60	40
Z-8	80	20

Table-1: Batch Composition

3.2 Raw Materials

3.2.1 Chemical Composition

Chemical compositions of the raw materials used in the preparation of samples are as follows (Table-2):-

	Zircon (%)	Dolomite (%)
SiO_2	34.35	3.6
ZrO_2	63.45	-

CaO	0.57	28.1
Al_2O_3	0.63	0.9
Fe_2O_3	0.16	0.5
TiO_2	0.44	-
MgO	-	18.2
Alkali	-	0.5
LOI	-	48.2

Table-2: Chemical Compositions of Raw Materials

3.2.2 Oxide Composition of Batches

Oxide compositions of the batches Z-2, Z-4, Z-6 and Z-8 prepared are as follows (Table-3):-

	Z-2 (wt. %)	Z-4 (wt. %)	Z-6 (wt. %)	Z-8 (wt. %)
SiO_2	9.75	15.9	22.05	28.2
ZrO_2	12.69	25.38	38.07	50.76
Al_2O_3	0.846	0.792	0.738	0.684
Fe_2O_3	0.432	0.364	0.296	0.228
TiO_2	0.088	0.176	0.264	0.352
CaO	24.194	18.288	12.268	6.476
MgO	16.16	12.12	8.08	4.04
Alkali	0.4	0.3	0.2	0.1
LOI	39.68	29.76	19.84	9.92

Table-3: Oxide Compositions of prepared batches

3.2.3 Batch Calculation

Based upon the percentage of Zircon and Dolomite in each batch composition, calculations were done for 50 grams for each batch (Table-4).

Batch	Zircon (grams)	Dolomite (grams)
Z-2	10	40
Z-4	20	30
Z-6	30	20
Z-8	40	10

Table-4: Batch Calculation for each composition

3.3 Sample Preparation

3.3.1 Mixing

For preparation of batch mixes of each of the batches, calculated amounts of each of the raw material (as per Table-4) was taken in a mortar & pestle, approximately 5 wt. % (3-4 drops) of 5% PVA solution was added as a binder and the entire mixture was mixed properly. Proper care was taken to avoid formation of agglomerates in the batch mix.

3.3.2 Pressing

Prepared batch mixes were divided into small parts and pressed into pellets (12.5mm die) at 3 tons for a dwell time period of 60 seconds using Carver Hydraulic Press machine.

3.3.3 Drying

After pressing, the pellets were air dried for 24 hours and then further dried in an oven at 110^{o}C for about 24 hours. After oven drying, dimensions and weight of the samples were measured with the help of a Vernier Caliper (least count = 0.02 mm) and a weighing machine respectively.

3.3.4 Firing

Three samples of each of the batches were taken and fired at 1300^{o}C, 1350^{o}C, 1400^{o}C and 1550^{o}C respectively with a soaking time period of two hours. After firing, the weight and dimensions of the samples were measured.

3.4 Sample Characterization

3.4.1 Volume Changes Measurement

Using the dimensional measurements, volume of the samples before and after firing process was calculated.

Let V_I = Initial Volume or volume of the sample before firing.

& V_F = Final Volume or volume of the sample after firing.

Then,

Volume change or $\Delta V = \{(V_F - V_I) / V_I\} * 100$

3.4.2 Apparent Porosity and Bulk Density Measurements

Due to the presence of CaO in the batch mixes, Apparent Porosity (A.P) and Bulk Density (B.D) determination was done in kerosene medium (to prevent hydration of CaO). A.P and B.D values were calculated by performing following steps:-

- Dry Weight (D) of the samples was measured.
- Samples were kept in a beaker half-filled with kerosene.

- The entire set-up was kept inside a vacuum desiccator until bubbles stopped coming out of the samples.
- Afterwards Suspended weight (S) and Soaked weight (W) of the samples were measured and A.P & B.D values were calculated.

$$\text{Apparent Porosity (A.P)} = \{(W-D) / (W-S)\}*100$$

$$\text{Bulk Density (B.D)} = \{D / (W-S)\}*\rho$$

Where ρ = Density of kerosene (~ 0.78)

3.4.3 Determination of Cold Crushing Strength (CCS)

Cold crushing strength of the samples was calculated with the help of a comprehensive tester by using the following formula:-

CCS = Load/Area

Load = Pressure at which the sample was crushed.

Area = Surface Area of the sample upon which load was applied (πr^2).

3.4.4 Phase Analysis

Phase analysis of the crushed samples was done with the help of an XRD (X-ray Diffractometer). XRD measurements were done in Philips X-Ray Diffractometer (PW 1730, Holland) at 2^o/min scan rate operated at 30 KeV and 20 mA. The crushed pieces of fired samples were grounded to a very fine powdered form in a mortar pestle. After X-ray analysis of the powdered samples, the analysis data was matched with the standard JCPDS software to identify the phases.

3.4.5 Microstructural Analysis

The microstructural analysis of the fractured surface was done with the help of SEM (Scanning Electron Microscope).

CHAPTER 4

RESULTS AND DISCUSSIONS

4. RESULTS AND DISCUSSION

4.1 Raw Material Characterization

Characterization of Zircon

Zircon characterization was done by X-Ray Diffraction method.

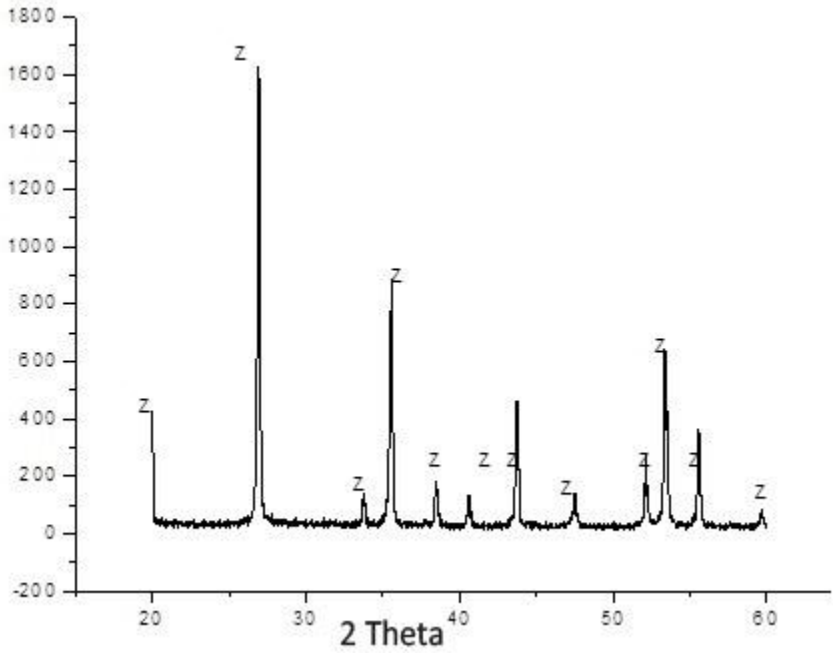

Fig-1: XRD Analysis of Zircon

XRD analysis of zircon as observed in (Fig-1) showed zircon present in high intensity peaks.

4.2 Sample Characterization

4.2.1 Apparent Porosity

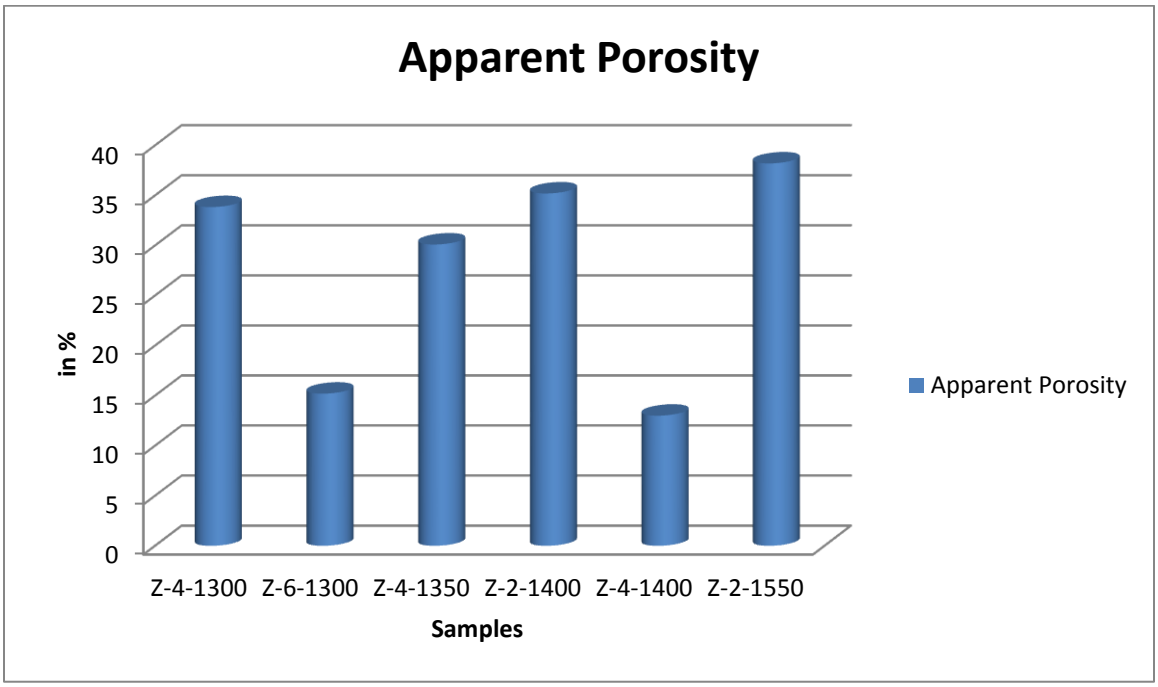

Fig-2: Apparent Porosity of the samples

Densification study of the samples was done through the measurement of apparent porosity and bulk density. Due to the wide variation in the compositions different characters was observed in different sintered samples. High dolomite containing samples were found to be sintered at low temperatures but on holding for few hours, they become crumbled automatically and converted to loose powders. This is due to the un-stabilization of calcined dolomite after firing and then getting hydrated in few hours after removal from furnace. Hence high firing temperature may be required for these samples for stabilization of dolomite by reaction with silica from zircon. Again at higher temperatures, high zircon containing samples is getting fused may due to the formation of fused mass in the system $CaO\text{-}MgO\text{-}SiO_2$.

4.2.2 Bulk Density

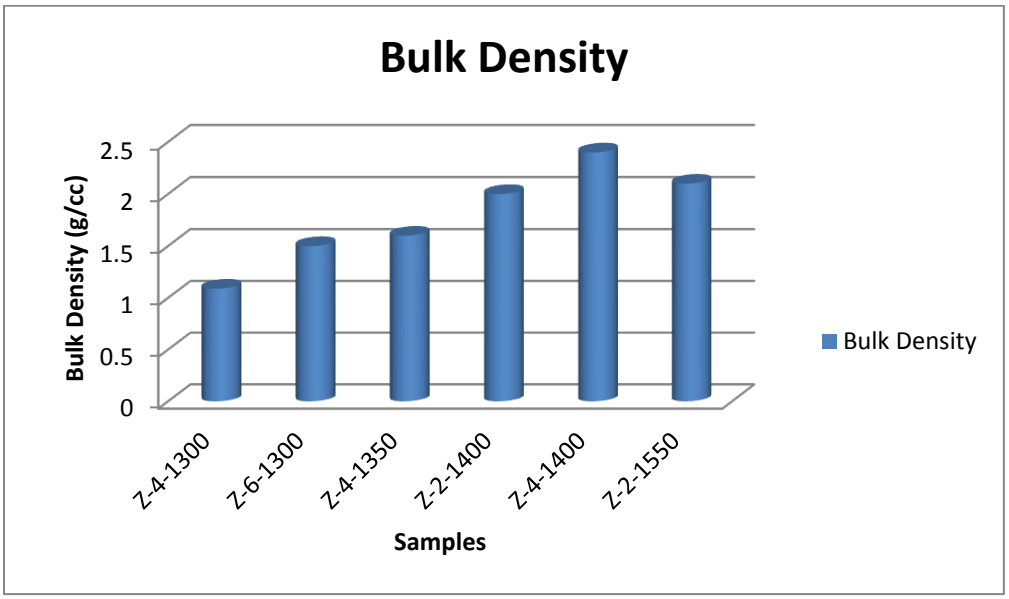

Fig-3: Bulk Density of the samples

4.3.3 Cold Crushing Strength

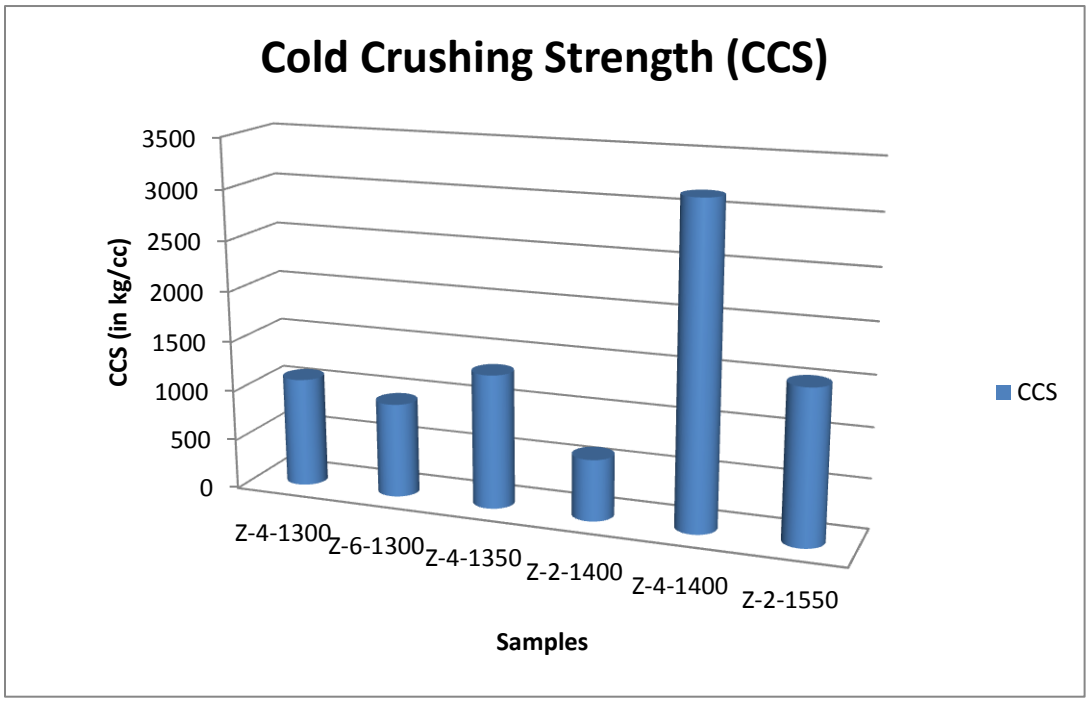

Fig-4: Cold Crushing Strength of the samples

4.3.4 XRD Phase Analysis

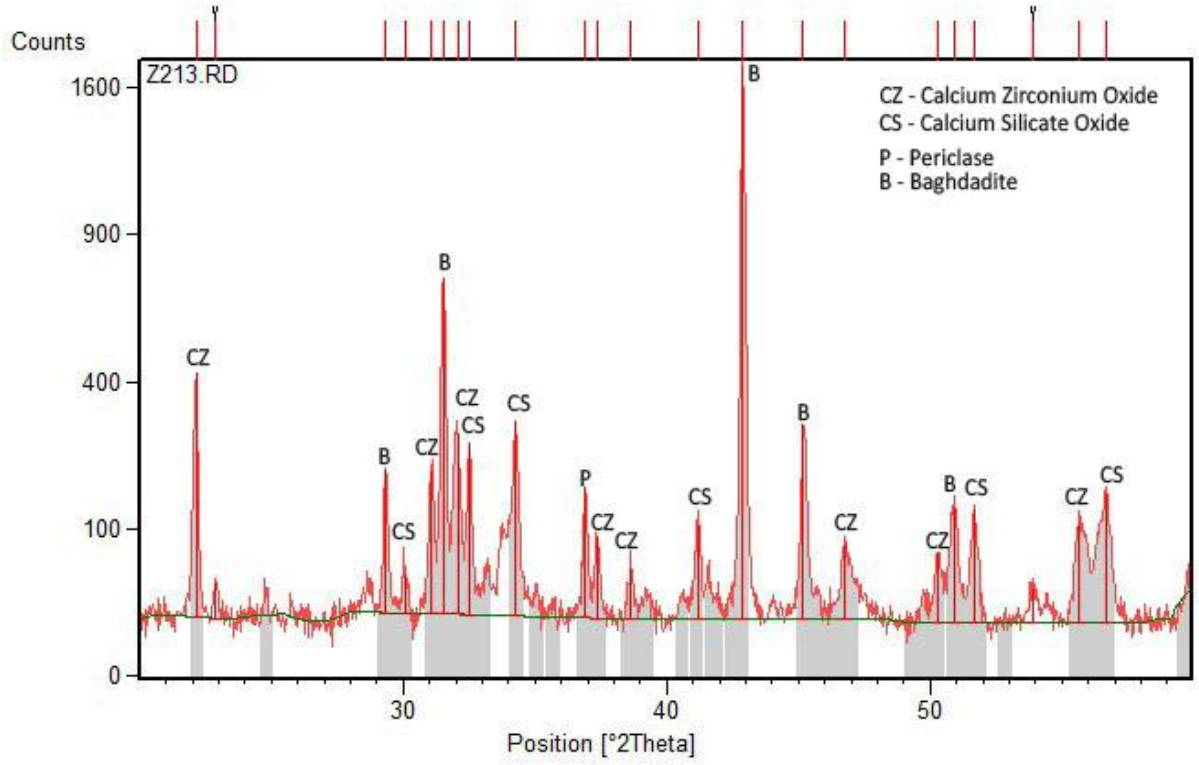

Fig-5: XRD Phase Analysis of Z-2 samples sintered at 1300°C

Main Phases observed in the XRD analysis of 20 wt. % Zircon containing samples (Z-2) as shown in Fig-6 & Fig-7 are as follows:-

- Calcium Zirconium Oxide ($CaZrO_3$).
- Periclase (MgO).
- Calcium Silicate Oxide (Ca_3SiO_5).
- Baghdadite ($Ca_3ZrSi_2O_9$).

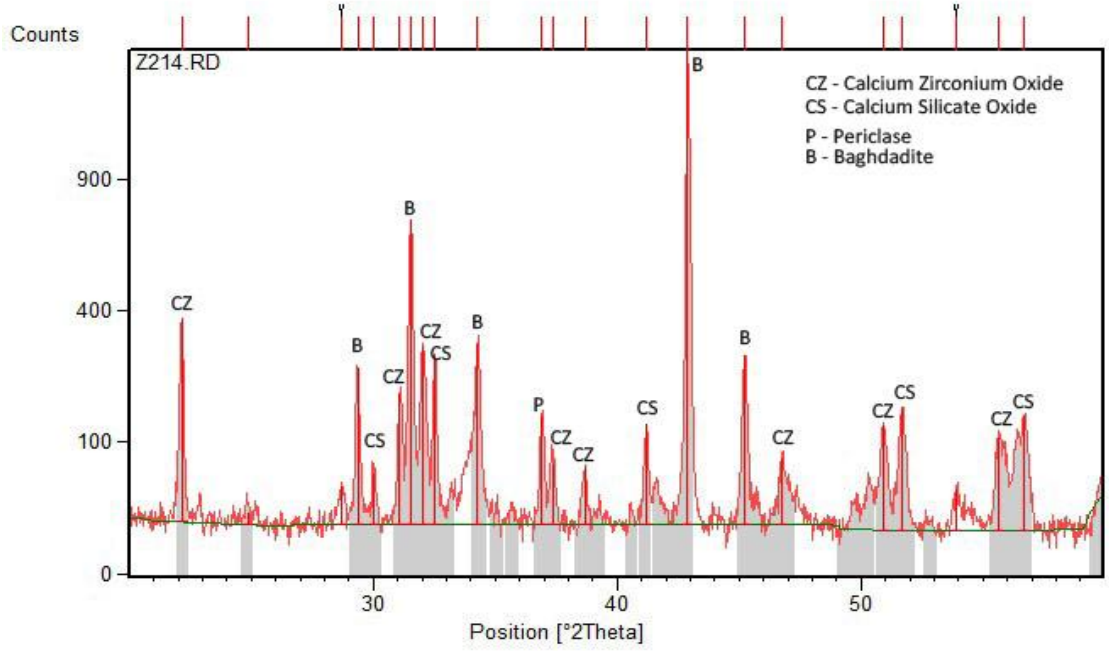

Fig-6: XRD Phase Analysis of Z-2 samples sintered at 1400°C

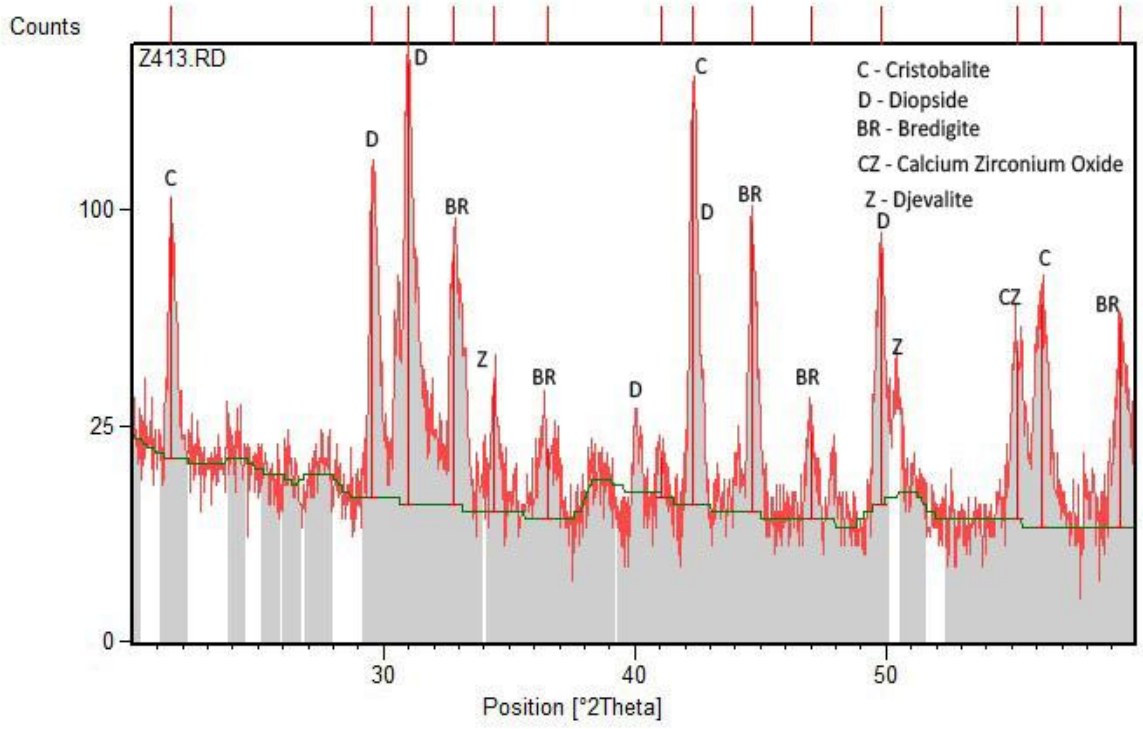

Fig-7: XRD phase Analysis of Samples sintered at 1300°C

Main Phases observed in the XRD analysis of 40 wt. % Zircon containing samples (Z-2) as shown in Fig-8 are as follows:-

- Calcium Zirconium Oxide (CaZrO3).
- Cristobalite (SiO_2).
- Djevalite ($Ca_{0.15}Zr_{0.85}O_2$).
- Bredigite ($Ca_7Mg(SiO_4)_4$).
- Diopside ($CaMgSi_2O_6$).

4.3.5 Microstructural Analysis

Microstructural analysis of the fractured surface was done by a Scanning Electron Microscope at 15 KV. 80% zircon containing samples (Z-8) were found to be melted at all the temperatures ranges from 1300 – 1550ºC and the microstructure was not found clearly. 20 wt. % zircon containing samples (Z-2) sintrered well but crumbled and converted to loose powder due to high presence of dolomite. Free lime, forming from dolomite and less stabilization due to lesser amount of silica from zircon, has resulted hydration and converted the samples to loose powders. Hence microstructure of these samples could not be done. As shown in Fig-9(a) and Fig-9(b), 40 wt. % Zircon containing samples (Z-4) showed relatively porous structure with not very clear grain boundaries and contours.

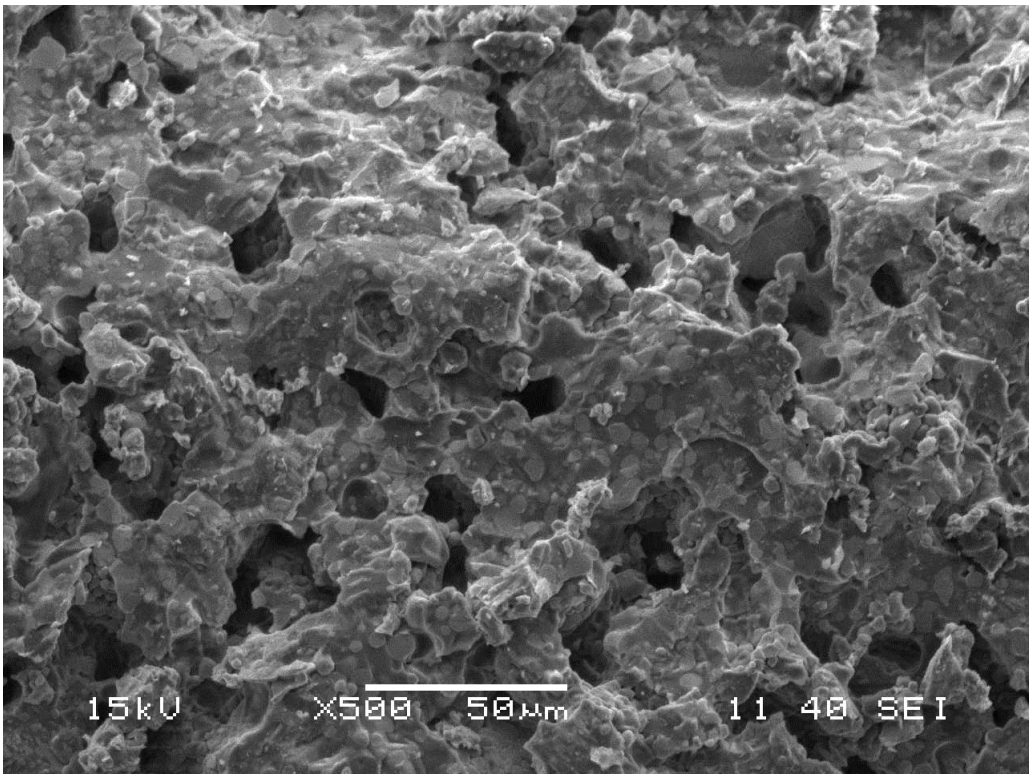

Fig-8(a): SEM micrograph of Z-4 sample sintered at 1300°C

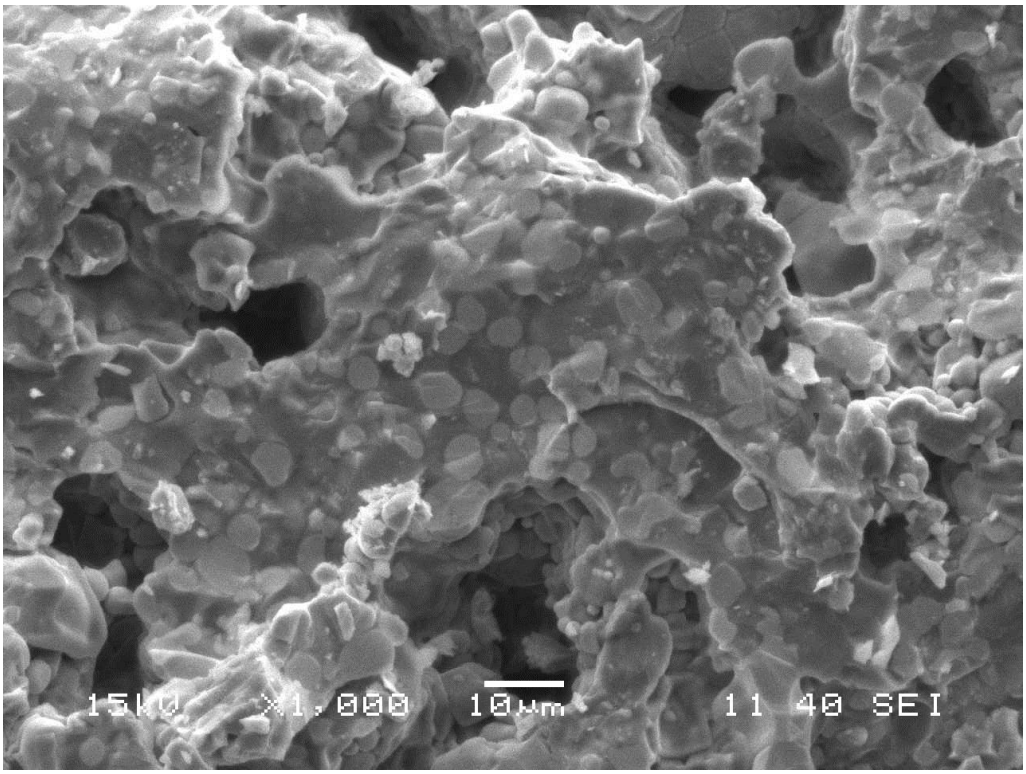

Fig-8(b): SEM micrograph of Z-4 sample sintered at 1300°C

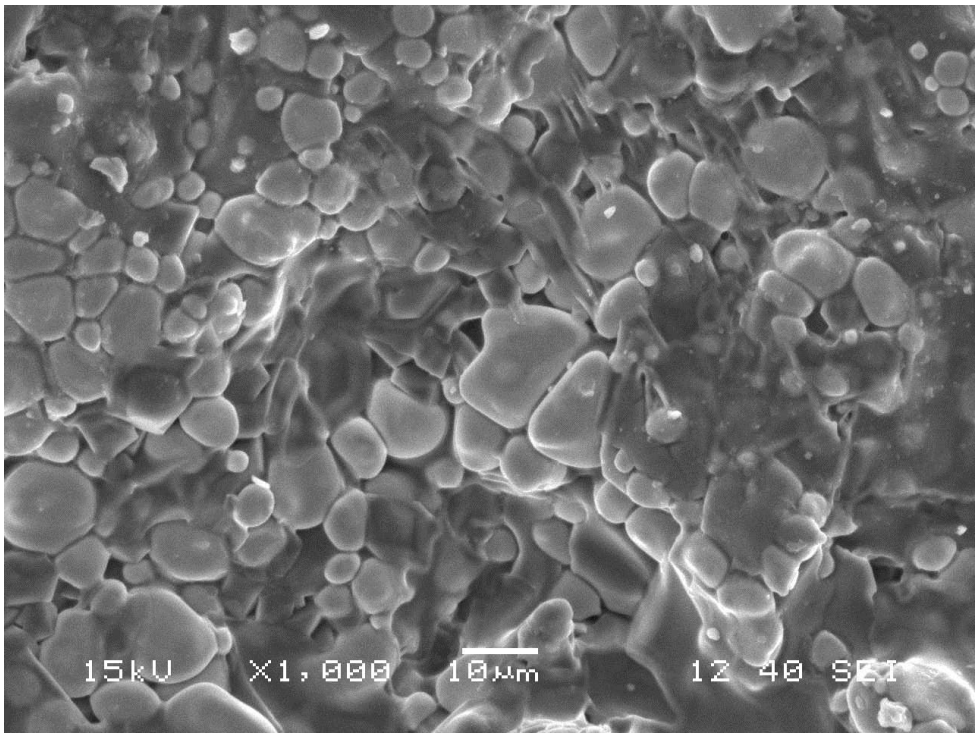

Fig-9(a): SEM micrograph of Z-6 sample sintered at 1300°C

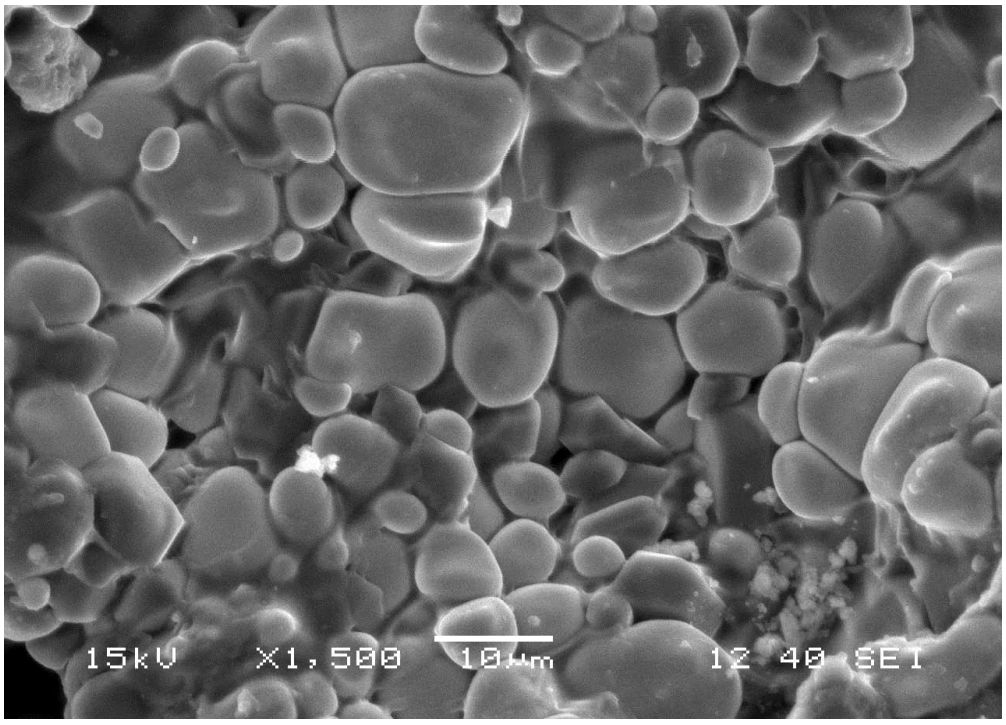

Fig-9(b): SEM micrograph of Z-6 sample sintered at 1300ºC

As shown in Fig-10(a) & Fig-10(b), 60 wt. % zircon containing samples (Z-6) showed very well densified samples and the microstructure showed well compacted grains, with non-angular smooth curved contours, indicating the liquid phase sintering of the products. The porosity level in the micrograpahs is also low, as observed in densification studies.

CHAPTER 5

SUMMARY

High dolomite containing samples were found to be sintered at low temperatures but on holding for few hours, they become crumbled automatically and converted to loose powders. This is due to the un-stabilization of calcined dolomite after firing and then getting hydrated in few hours after removal from furnace. Again at higher temperatures, high zircon containing samples is getting fused may due to the formation of fused mass in the system CaO-MgO-SiO_2.In the XRD phase analysis of 20% Zircon containing samples, the main phases observed were Calcium Zirconium Oxide ($CaZrO_3$), Periclase (MgO), Calcium Silicate Oxide (Ca_3SiO_5), Baghdadite ($Ca_3ZrSi_2O_9$). While in the XRD analysis of 40% Zircon containing samples, the main phases observed were Calcium Zirconium Oxide (CaZrO3), Cristobalite (SiO_2), Djevalite ($Ca_{0.15}Zr_{0.85}O_2$), Bredigite ($Ca_7Mg(SiO_4)_4$), Diopside ($CaMgSi_2O_6$). 40 wt. % Zircon containing samples showed relatively porous structure with not very clear grain boundaries and contours during microstructural analysis, while 60 wt. % zircon containing samples showed very well densified samples and the microstructure showed well compacted grains, with non-angular smooth curved contours, thus indicating the liquid phase sintering of the products.

CHAPTER 6

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6. REFERENCES

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